

# Single Molecule Spectroscopy as a possible tool to study the electric field in superconductors

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**Abstract.** – We discuss the influence of the superconducting transition in a film on the fluorescence spectrum of a single molecule located nearby. We show that single molecule spectroscopy (SMS) should be an appropriate tool to detect the electric charge associated with a vortex line. Also we argue that an electric field must appear at the boundaries between normal and superconducting regions of the intermediate phase and SMS could be useful to study this effect.

*Introduction.* – The studies of the electric field effects in superconductors have a rather long history (see Ref. [1] and articles cited there). In spite of a large number of theoretical works there exist only a few experimental hints on the experimental observation of electric field in superconductors. A regain of interest to this subject has been stimulated by the prediction of the existence of an electric charge of the vortex core (see Ref. [2]). It was argued there that the vortex charge can be responsible for the sign change in the Hall effect below  $T_c$ . Subsequent studies [3] stressed the importance of the metallic screening which strongly reduces the vortex core charge. For the moment, there is no direct experimental evidence of the charge of a single vortex. Note that high-resolution nuclear quadrupole frequency measurements revealed a change in the local electric field at the transition into the mixed state in YBaCuO [4]. However, this behavior can also be explained by a magnetostriction effect due to the coupling between the vortex lattice and the crystal structure. Therefore, it remains of considerable interest to directly observe the charge of a single vortex.

Another interesting example of electric field generation in a superconductor is the intermediate state in type I material. This state involves a sequence of normal and superconducting regions and appears for example in superconducting films submitted to a perpendicular magnetic field. The electric charge in this case appears at the boundaries between the normal and

superconducting phases. The electric field in the intermediate state outside the superconductor decreases more slowly with the distance from the surface compared to the vortex field, which can facilitate its registration.

In this paper, we will show that single-molecule spectroscopy [5] should provide a very sensitive probe for the charge distribution and electric fields in superconductors. Free from ensemble averaging, small shifts of the narrow single molecule optical lines induced by an external perturbation can be measured with high accuracy at liquid Helium temperatures. This technique has been successfully used to probe the dynamics of low-energy excitations (two-level systems) in polymers [6] and to reveal interesting phenomena in the electric conduction of semi-conductors [7]. Therefore it may be quite appropriate to perform the challenging experiments on the observation of the electric charge of a single vortex or of the domain wall charge in the intermediate superconducting state.

Single molecule lines being unaffected by the modest magnetic field of the vortex, the SMS will thus selectively feel the electric charge associated to the vortex and will be complementary to the decoration and STM techniques of vortex imaging.

*Single Molecule Spectroscopy.* – Single molecule spectroscopy is based on the detection of the laser-induced fluorescence from a small volume of a solid matrix doped with highly fluorescent molecules, in which at most one and only one chromophore molecule can be excited by the laser [8]. As the red-shifted fluorescence photons can be efficiently separated from stray laser photons scattered from the intense exciting beam, the weak single molecule signal appears on a very low background, with a high signal-to-noise ratio. At liquid helium temperatures, the zero-phonon lines of the electronic component (0-0 vibronic line) of a single molecule can become extremely narrow, while the center frequencies of different molecules are still spread over a broad inhomogeneous band [9]. The inhomogeneous broadening arises from the many defects in the solid matrix, which shift single-molecule lines at random. Therefore, for each particular laser frequency, resonance is achieved only for a very small fraction of the molecules in the sample. In addition to the spatial selection (use of small excitation volumes of tightly focused beams), the laser thus selects molecules spectrally too.

At low temperatures the dephasing of the optical transition dipole due to phonons vanishes. For few well chosen fluorophores-matrix systems, such as the polycyclic aromatic chromophores (dibenzo-anthanthrene or Terrylenne) embedded in a molecular crystal (Naphtalene,...) or n-Hexadecane Shpol'skii matrix, the narrow zero-phonon line has a spectral width limited by the lifetime of the molecule excited state ( $\sim 10$ -40 MHz). This allows one to employ single chromophore molecules as highly sensitive probes for their local nano-environments. Internal processes, and external perturbations, which shift the resonance frequency of a single molecule on the order of  $10^{-7}$  of the absolute optical frequency, are easily detectable.

An external electric field changes the spectral position of the molecular transition by:

$$\Delta\nu = -\frac{1}{\hbar} \left( \delta \vec{p} \cdot \vec{E}_{loc} + \frac{1}{2} \vec{E}_{loc} \cdot \delta \overleftrightarrow{\alpha} \cdot \vec{E}_{loc} \right), \quad (1)$$

where  $\delta \vec{p}$  is the difference between the dipole moment vectors and  $\delta \overleftrightarrow{\alpha}$  the difference between the tensors of electrical polarizability between the excited and ground state of the molecule.  $\vec{E}_{loc}$  is the local electrical field. Centrosymmetric molecules such as dibenzo-anthanthrene and terrylene exhibit only a quadratic Stark effect in a vacuum, but when embedded in a solid matrix, they usually gain a permanent dipole moment due to distortions by the surrounding matrix. This leads to an additional linear contribution to the Stark shift, which is usually much stronger than the quadratic shift. In strongly disordered matrices such as polymers,  $\delta \vec{p}$  can be as large as  $1D$  (Debye), but it is around  $0.3D$  in n-Hexadecane Shpol'skii matrix

(corresponding to the frequency shift  $\sim 2 \text{ MHz}/(\text{kV}/\text{m})$ ) [10]. Thus local electric fields of  $\sim 10 \text{ kV}/\text{m}$  will induce a shift of a single dibenzo-anthanthrene line of the order of its width ( $\sim 20 \text{ MHz}$ ).

Zeeman shift of the singlet-singlet transition of planar aromatic molecule line is extremely small [11]. Since the molecule has no permanent magnetic moment, the shift is quadratic and is less than  $-80 \text{ MHz}/\text{T}^2$ . This means that single molecules line are unaffected by moderate magnetic fields such as that created by vortex in its neighborhood.

*Detection of a single vortex charge by single molecule spectroscopy.* – In this section, we briefly remind of the mechanism of the generation of the charge associated with a vortex line (for more details, see Ref. [3]). The geometry of the studied system is displayed in Fig. 1. The molecule is supposed to be at the distance  $z_0$  from the superconducting film (because of the presence of the solid matrix).

The transition into a superconducting state changes the energy spectrum near the Fermi-level and leads to a variation of the chemical potential  $\mu$  as  $\delta\mu \sim -\Delta^2/\mu_0$  (see [2]) where  $\Delta$  is the superconducting energy gap and  $\mu_0$  is the chemical potential in the normal state. The particle-hole asymmetry also gives a contribution to  $\delta\mu$  of the same order of magnitude [3]. We consider below the vortices in type II superconductors and the intermediate state in type I superconductors. In both cases the system comprises a normal (the vortex core for the type II superconductor) and a superconducting parts. The equality of the electrochemical potentials leads to the electrical charge redistribution between normal and superconducting regions. Indeed, the energy gain due to the condensation of pairs lowers the energy of the charge carriers and then provokes some carrier influx from the normal region.

Following Ref. [3] the spatial variation of the gap near the vortex core can be modelled by  $\Delta^2(\rho) = \Delta_0^2/(\rho^2 + \xi^2)$ . Then, the charge variation will be (for  $\rho \ll \lambda$ , where  $\lambda$  is the penetration depth)

$$\delta q_{ext} = \frac{KeN(\mu_0)\Delta_0^2\rho^2}{\mu_0(\rho^2 + \xi^2)}, \quad (2)$$

where the coefficient  $K$  is of the order of unity and depends on the details of the electronic band structure. However, this charge redistribution is strongly screened; in the Thomas-Fermi approximation the electrostatic potential  $\varphi(\vec{r})$  in the superconductor may be determined from

$$(\nabla^2 - \frac{1}{\lambda_{TF}^2})\varphi(\vec{r}) = -4\pi\delta q_{ext}. \quad (3)$$

In the limit  $\xi \gg \lambda_{TF}$  the potential in the first approximation is  $\varphi(\vec{r}) = 4\pi\lambda_{TF}^2\delta q_{ext}$  and the resulting charge density  $\delta q$  may be obtained from the Poisson equation  $\nabla^2\varphi(\vec{r}) = -4\pi\delta q$ . We see that the electrostatic screening strongly reduces the "bare" charge redistribution and may be determined from  $\delta q = -\lambda_{TF}^2\nabla^2(\delta q_{ext})$ .

Outside the sample the electrostatic potential is maximal on the vortex axis and given by

$$\varphi_{out} = -\frac{8\pi K\lambda_{TF}^2\xi^2eN(\mu_0)\Delta_0^2}{\mu_0} \int_0^\infty \int_0^\infty dz\rho d\rho \frac{\xi^2 - \rho^2}{(\rho^2 + \xi^2)^3 \sqrt{\rho^2 + (z + z_0)^2}}, \quad (4)$$

where  $z_0$  is the coordinate of the molecule on the  $z$  axis. The electrical field can then be deduced from the above expression. The component of the electric field along the  $z$  axis

denoted  $E_z$  is

$$E_z = -\frac{\partial \varphi_{out}}{\partial z_0} \quad (5)$$

$$= \frac{4\pi K \lambda_{TF}^2 e N(\mu_0) \Delta_0^2}{\mu_0 \xi} \int_0^\infty du \frac{u-1}{(u+1)^3 \sqrt{u+a}}. \quad (6)$$

where  $u = (\rho/\xi)^2$  and  $a = (z_0/\xi)^2$ . In the case  $z_0 > \xi$  ( $a > 1$ ),  $E_z$  becomes

$$E_z = \frac{4\pi K \lambda_{TF}^2 e N(\mu_0) \Delta_0^2}{\mu_0 \xi} \left[ \frac{3\sqrt{a}}{2(a-1)^2} - \frac{(2a+1)}{2(a-1)^{5/2}} \ln(\sqrt{a} + \sqrt{a-1}) \right]. \quad (7)$$

Note that in the case  $a < 1$ , the expression of  $E_z$  is a bit more complicated, and therefore not presented here.

When the molecule is far from the vortex (that is  $z_0 \gg \xi$ ),  $E_z$  can be simplified into

$$E_z \approx -\frac{4\pi K \lambda_{TF}^2 e N(\mu_0) \Delta_0^2}{\mu_0 \xi} \left[ \left( \frac{\xi}{z_0} \right)^3 \ln \frac{z_0}{\xi} \right], \quad (8)$$

which corresponds to the asymptotic formula obtained in Ref. [3]. Note that this formula is valid for  $z_0 < \lambda$ , otherwise  $z_0$  has to be replaced by  $\lambda$  in the logarithm term in (8). The electric field at the surface of superconductor ( $z_0 = 0$ ) as it readily follows from expression (6) is

$$E_z(0) = -\frac{\pi^2 K \lambda_{TF}^2 e N(\mu_0) \Delta_0^2}{\mu_0 \xi}. \quad (9)$$

At the surface of the superconductor, the electric field created by the charge associated to the vortex core (6) depends on the temperature following the ratio  $\Delta_0^2/\xi$ . More precisely, since  $\Delta_0^2 \sim (T_c - T)$  and  $\xi \sim (T_c - T)^{-1/2}$ , the evolution of  $E_z$  as a function of temperature is given by  $(T_c - T)^{3/2}$ . Therefore, the electric field effect quickly disappears when the temperature approaches the critical temperature. In other words, the experiment should better be performed at sufficiently low temperature ( $T \lesssim 0.5T_c$ ). At large distances,  $z_0 \gg \xi$ , the temperature dependence is given by  $\Delta_0^2 \xi^2$ . However, this coefficient does not depend on the temperature, and, as a result, so does  $E_z$ . Therefore, the variation of the electric field as a function of the temperature depends on the thickness of the solid matrix containing the studied molecule.

One can notice from expression (8) that the vortex electric field, and as a result the detected effect, rapidly decreases as a function of the distance between the molecule and the vortex ( $\sim z_0^{-3}$ ). The thickness of the solid matrix should therefore be as thin as possible. One can roughly estimate the value of the electric field at the surface of the superconducting vortex considering expression (9):  $E_z(0) \sim e/(\xi a_B)(T_c/\mu_0)^2$ . The parameter  $a_B$  is the Bohr radius and is about 0.1 nm. If the superconducting coherence length  $\xi$  is 10 nm and  $T_c/\mu_0 \sim a_B/\xi$ , then  $E_z(0) \sim e a_B/(\xi^3) \sim 10^5$  V/m, which is of the same order of magnitude as the SMS sensitivity.

From an experimental point of view it is unlikely that the fluorescent molecule will be just above the vortex. It may be then more appropriate to change the external magnetic field, which would make the vortices move. In such a setup is possible to detect the movement of the vortex when it passes below the SMS molecule. However the distance  $z_0$  between the fluorescent molecule and superconductor needs to be smaller than the period  $a_A$  of the Abrikosov lattice. For  $z_0 > a_A$  the amplitude of the electric field modulation decreases exponentially as  $\exp(-2\pi z_0/a_A)$  [3].

*Intermediate state.* – The system studied in this section is a film in the so-called intermediate state, as shown in Fig. 2. The intermediate state appears in type I superconducting films when a perpendicular magnetic field is applied. In this state, regions of normal and superconducting Meissner phases alternate. The  $x$  axis is chosen perpendicular to the S/N boundary (located at  $x = 0$ ). The N state occupies the space where  $x < 0$  while the S state corresponds to  $x > 0$ .

In the intermediate state, the form of the order parameter variation can be extrapolated from the Ginzburg Landau theory [14] to the low temperatures as  $\Delta(x) = \Delta_0 \tanh(x/\sqrt{2}\xi)$ . Taking into account the metallic screening, the charge density being

$$\delta q = \frac{K\lambda_{TF}^2 e N(\mu_0) \Delta_0^2}{\mu_0 \xi^2} \left( \frac{3}{\cosh^4(x/\sqrt{2}\xi)} - \frac{2}{\cosh^2(x/\sqrt{2}\xi)} \right). \quad (10)$$

As in the previous section, the electric field created above the superconductor can be deduced from the expression of the potential resulting from the density charge (10). If the molecule is located at the coordinates  $x_0$  and  $z_0$ , the components of the electric field may be written as

$$E_z = \frac{K\lambda_{TF}^2 e N(\mu_0) \Delta_0^2}{\mu_0 \xi^2} \int_0^\infty \int_{-\infty}^\infty \int_0^\infty \frac{dx dy dz (z + z_0)}{\left( (x - x_0)^2 + (z + z_0)^2 + y^2 \right)^{3/2}} \left( \frac{3}{\cosh^4 \frac{x}{\sqrt{2}\xi}} - \frac{2}{\cosh^2 \frac{x}{\sqrt{2}\xi}} \right), \quad (11)$$

$$E_x = \frac{K\lambda_{TF}^2 e N(\mu_0) \Delta_0^2}{\mu_0 \xi^2} \int_0^\infty \int_{-\infty}^\infty \int_0^\infty \frac{dx dy dz (x_0 - x)}{\left( (x - x_0)^2 + (z + z_0)^2 + y^2 \right)^{3/2}} \left( \frac{3}{\cosh^4 \frac{x}{\sqrt{2}\xi}} - \frac{2}{\cosh^2 \frac{x}{\sqrt{2}\xi}} \right) \quad (12)$$

At large distances  $\frac{z_0}{\sqrt{2}\xi} \gg 1$ , we have

$$E_z \approx -\frac{\lambda_{TF}^2 e K N(\mu_0) \Delta_0^2}{\mu_0 \xi} \sqrt{2} \frac{\tilde{x}_0 - 1}{(\tilde{z}_0)^2}, \quad (13)$$

where  $\tilde{x}_0 = \frac{x_0}{\sqrt{2}\xi}$ . The decrease of  $E_z$  in the intermediate state is slower than in the vortex case ( $\sim \tilde{z}_0^{-3}$ ).

The component  $E_x$  of the electric field parallel to the surface decreases even more slowly, as  $E_x \sim \tilde{z}_0^{-1}$ . Indeed, at large distances  $\tilde{z}_0 \gg 1$ , it can be written as

$$E_x \approx -\frac{\sqrt{2}\lambda_{TF}^2 K e N(\mu_0) \Delta_0^2}{\mu_0} \frac{1}{z_0}. \quad (14)$$

Note that  $E_x$  depends on the temperature as  $T_c - T$ . At the surface of the superconductor, if the molecule is above the N region ( $\tilde{x}_0 < 0$ ),  $E_x = 0$  while if it is above the S state ( $\tilde{x}_0 > 0$ ),  $E_x$  can be expressed as

$$E_x \approx \frac{\lambda_{TF}^2 K e N(\mu_0) \Delta_0^2}{\mu_0 \xi} 8\sqrt{2}\pi \frac{e^{2\tilde{x}_0} (e^{2\tilde{x}_0} - 1)}{(e^{2\tilde{x}_0} + 1)^3}. \quad (15)$$

Note that the maximum field is achieved at  $\tilde{x}_0 = \ln(2 + \sqrt{3})/2 \approx 0.66$  and is equal to  $E_x^{\max} = \frac{\lambda_{TF}^2 e K N(\mu_0) \Delta_0^2}{\mu_0 \xi} c$  ( $c = 4\pi\sqrt{2}/3\sqrt{3}$ ). In this case, the temperature dependence is

$(T_c - T)^{3/2}$ . An estimate of an electric field above the S/N interface gives the field of same order of magnitude as above the vortex core. Therefore the SMS could detect the electric field in the intermediate state too.

*Conclusion.* – We have argued that single molecule spectroscopy may be a useful tool to study the electric field effects in superconductors. The order of magnitude of the electric field above the vortex core or near the S/N interface in the intermediate state is about  $10^5$  V/m for a distance of  $\sim 10$  nm, is one order of magnitude larger than the limit of electric field detection by Stark-shift of single molecule lines. Because of metal quenching [12], [13] (which induces fluorescence intensity decrease and line-broadening), molecule-superconductor-substrate distances should be larger than 20 nm. At these distances, charge distributions at the S/N interface are still detectable (because of the  $1/z_0$  decrease of the field). However for vortices one can rapidly reach the sensitivity limit of electric field detection (due to  $1/z_0^3$  decrease of the field).

To improve the sensitivity, one can use very thin layers of superconductors to limit the metal quenching effects. Another possibility would be to apply a time modulated magnetic field or electric current to the superconductor. This will induce an oscillation of the molecule-vortex (or S/N interface) distance and thus a modulation of the single molecule resonance position. When the molecule is excited at a fixed laser wavelength, detecting the fluorescence intensity fluctuations at the magnetic field (electric current) modulation frequency can improve the sensitivity by more than one order of magnitude and thus ensure an accurate estimation of the electric field effects.

Among the perspectives of the SMS method, we should mention the study of the dynamics of the vortex flow and S/N boundary displacements in the intermediate phase. Also if the SMS sensitivity could be increased, this method could be applied to study such a subtle effect as the Bernoulli potential in the Meissner state (see for example [16]).

Finally note that even in the absence of vortices or intermediate state the superconducting transition may influence SMS spectra. Indeed the transition into the superconducting state leads to a change of the permittivity [15]  $\delta\epsilon/\epsilon \sim \Delta^2/\omega^2 \ln(\omega/\Delta)$ , in the limit  $\omega \gg \Delta$ , as it is realized in the experimental situation. The modification of the permittivity leads to a shift in the fluorescence frequency due to dipole mirror image charge effect. The change of the frequency is however quite small and may be of some relevance only for high- $T_c$  superconductors or in the case of the fluorescence in the near infrared. One may also expect that the superconducting transition could significantly modify the decay rate of the single molecule fluorescence.

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